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Inorganica Chimica Acta

# Contents

## Articles

**F. Abbate, P. Orioli, B. Bruni, G. Marcon, L. Messori**

*Inorg. Chim. Acta 311 (2000) 1*

Crystal structure and solution chemistry of the cytotoxic complex 1,2-dichloro(*o*-phenanthroline)-gold(III) chloride

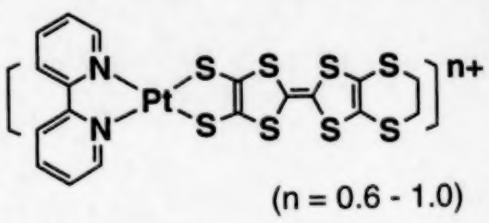
The crystal structure of the cytotoxic complex 1,2-dichloro(*o*-phenanthroline)gold(III) chloride ([AuphenCl$_2$]Cl) is reported; the complex is square planar and exhibits a regular geometry. The behavior in solution of [AuphenCl$_2$]Cl was further investigated by $^1$H NMR spectroscopy.

**Kazuya Kubo, Motohiro Nakano, Hatsue Tamura, Gen-etsu Matsubayashi**

*Inorg. Chim. Acta 311 (2000) 6*

Preparation of Pt(II) and Pd(II) complexes coordinated with both a diimine ligand and a sulfur-rich dithiolate ligand and electrical conductivities of their oxidized species and X-ray crystal structure of Pd(*N*-butyl-pyridine-2-carbaldimine)($C_3S_5$)

Pt(L)($C_8H_4S_8$) [L = 2,2′-bipyridine (bpy) and *N*-butyl-pyridine-2-carbaldimine (Bu-pya)], Pt(bpy)-(C10–$C_6S_8$) [C10–$C_6S_8^{2-}$ = 2-{bis(dodecylthio)-1,3-dithiole-2-ylidene}-1,3-dithiole-4,5-dithiolate (2−)], Pd(Bu-pya)($C_8H_4S_8$), and Pd(Bu-pya)($C_3S_5$) were prepared. They were oxidized by $I_2$ or TCNQ to afford [Pt(L)($C_8H_4S_8$)]($I_3$)$_x$ ($x$ = 0.9–1.0), [Pt(L)($C_8H_4S_8$)](TCNQ)$_y$ ($y$ = 0.6–0.8) (L = bpy, Bu-pya and C10–$C_6S_8$) and [Pd(Bu-pya)($C_8H_4S_8$)]·$I_{5.1}$ and [Pd(Bu-pya)($C_8H_4S_8$)](TCNQ)$_{0.4}$. Some of them exhibited electrical conductivities of $10^{-3}$ S cm$^{-1}$ measured for compacted pellets at room temperature. The X-ray crystal structure of Pd(Bu-pya)($C_3S_5$) was determined.

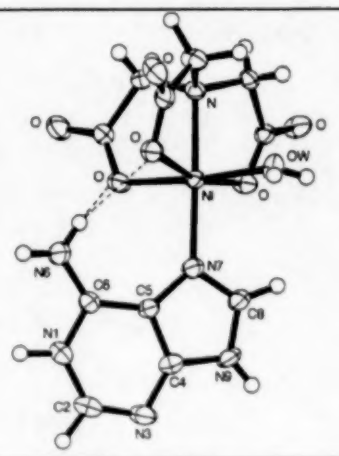



**Md. Abdus Salam, Katsuyuki Aoki**

*Inorg. Chim. Acta 311 (2000) 15*

Interligand interactions affecting specific metal bonding to nucleic acid bases: the tripodal nitrilotriacetato (nta) ligand-system. Crystal structures of [(nta)(adeninium)(aqua)nickel(II)] hydrate, [(nta)-(diaqua)nickel(II)]·(cytosinium) hydrate, and [(nta)(diaqua)nickel(II)]·(cytosinium)·(cytosine) hydrate

Treatment of Ni(OAc)$_2$ and nitrilotriacetic acid ($H_3$nta) with adenine, 9-ethylguanine, cytosine, or uracil, yields a metal complex only for adenine, [Ni(nta)(adeninium)-($H_2O$)]$_2$·5$H_2O$ (**1**), the structure of which was determined by X-ray diffraction. Adenine through N(7)-specific metal bonding of the [Ni(nta)($H_2O$)]$^-$ species is caused by the formation of interligand hydrogen bonds between N(6) and carboxylato oxygens.

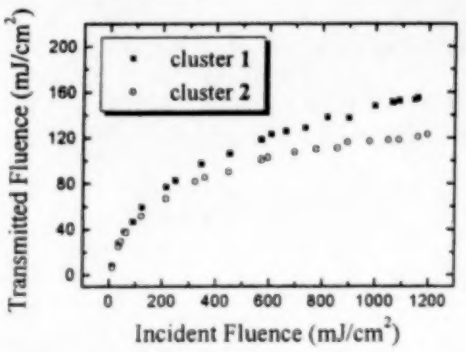



**Chi Zhang, Yinglin Song, Yan Xu, Guocheng Jin, Guangyu Fang, Yuxiao Wang, Hoongkun Fun, Xinquan Xin**

*Inorg. Chim. Acta 311 (2000) 25*

Two interesting heterobimetallic compounds [$MOS_3Cu_3$(4-pic)$_6$]·Br (M = Mo, W) with cationic cluster: synthesis, structural characterization, nonlinear response and large optical limiting properties

Two heterobimetallic compounds [$MOS_3$-$Cu_3$(4-pic)$_6$]·Br (M = Mo, W) with a cationic cluster skeleton are unusual in comparison with the analogical nest-shaped clusters with a neutral or anionic skeleton, possessing large optical limiting properties, strong nonlinear absorption and self-focusing effects.

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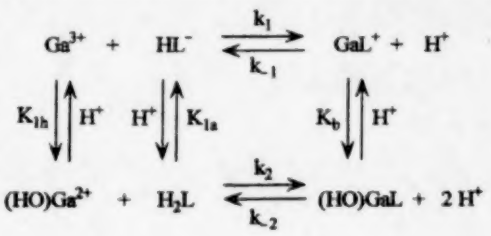
**C.J. Macdonald**

*Inorg. Chim. Acta 311 (2000) 33*

The complexation reaction of gallium(III) with 4-nitrocatechol: evidence for a dissociative-interchange mechanism on $(H_2O)_5Ga(OH)^{2+}$

In aqueous solution in the pH range 2–3, excess $Ga^{3+}$ reacts with 4-nitrocatechol ($H_2L$) to give the monochelate, $GaL^{+}$. Excellent agreement is found between the spectrophotometrically and kinetically determined values of $K_c$ at 25°C and $I = 0.1$ M. Complex formation involves reaction between the monohydroxo ion, $(H_2O)_5Ga(OH)^{2+}$, and undissociated ligand. The kinetic data are consistent with the $I_d$ mechanism for ligand substitution.

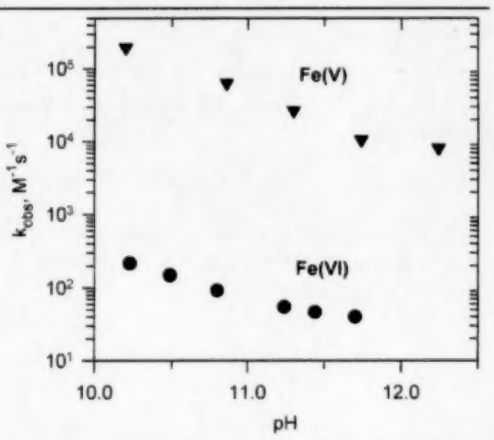



**Virender K. Sharma, Donald B. O'Connor**

*Inorg. Chim. Acta 311 (2000) 40*

Ferrate(V) oxidation of thiourea: a premix pulse radiolysis study

A premix pulse radiolysis technique was used to study the oxidation of thiourea by Fe(V) as a function of pH (10.20–12.24). The reactivity of Fe(V) with thiourea is three orders of magnitude faster than with Fe(VI). Fe(V) reacts preferentially at the sulfur center of thiourea.

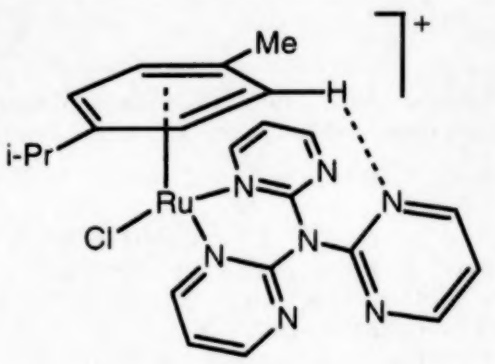



**Wenbin Yao, Konstantinos Kavallieratos, Susan de Gala, Robert H. Crabtree**

*Inorg. Chim. Acta 311 (2000) 45*

Dipyrimidylamine and tripyrimidylamine as chelating N-donor ligands

Di- and tri-pyrimidylamine (dipm, tripm) are synthesized. The tripm Ru(II) complex shown has a C–H···N hydrogen bond. The Tolman electronic parameter is determined for dipm from $[(dipm)Mo(CO)_4]$ IR data.

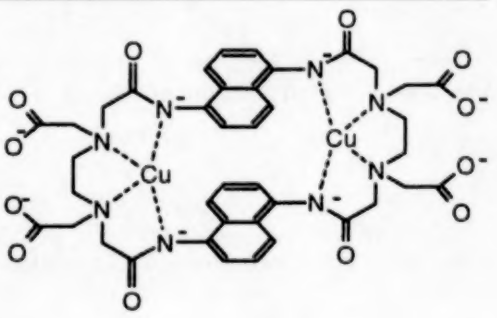



**Michiko B. Inoue, Iliana C. Muñoz, Lorena Machi, Motomichi Inoue, Quintus Fernando**

*Inorg. Chim. Acta 311 (2000) 50*

Structural and spectroscopic studies of binuclear $Cu^{2+}$ and $Co^{2+}$ complexes with an amide-based naphthalenophane

X-ray studies of binuclear $Cu^{2+}$ and $Co^{2+}$ complexes with an amide-based naphthalenophane indicate that the coordination of amide groups defines the coordination geometries and leads to distortion of the aromatic groups from the planar structure. The influence of the π-electron system by metal complexation is observed as a change in the absorption and luminescence spectra.

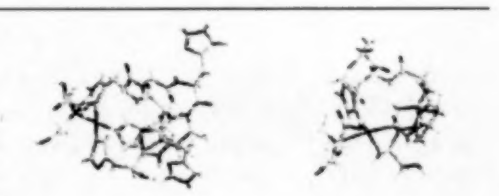



**Matthew S. Ward, Rex E. Shepherd**

*Inorg. Chim. Acta 311 (2000) 57*

Comparison of energy-minimized structures of $[Pd^{II}(mida)]$ complexes of peptide sequences used in immobilized metal ion affinity chromatography protein separations

Molecular mechanics methods show that $[Pd^{II}(mida)L_3]$ complexes ($mida^{2-}$ = *N*-methyliminodiacetate) have the lowest energy for an N-ligand set of (imidazole)$_2$(amine) for amino acid side chain donors. Upon chelation, the $[Pd^{II}(mida)$(hexamer peptides)] follow an energy-minimization order of $G_6$ (peptido coordinated; most stable) < $imH_4G_2$ (three im from histidine) < $imH_6$ < GH*PH*H*G (* three histidyl donors) < S*PH*H*GG (* amine plus * two histidyl donors) ≪ $amH_4G_2 \sim amH_6$ (amine plus two histidyl donors; least stable). Spartan, MMFF94 and SYBYL perform better than MM2-level calculations in predicting aspects of peptide binding for immobilized metal ion affinity chromatography protein separations.



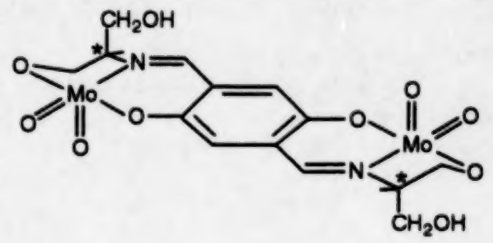
**IMAC peptide anchors : $(His)_6$ and SPHHGG coordinated to an iminodiacetate metal binding site**

**Masato Kato, Kiyohiko Nakajima, Yuzo Yoshikawa, Masakazu Hirotsu, Masaaki Kojima**

*Inorg. Chim. Acta 311 (2000) 69*

Preparation and properties of dinuclear dioxomolybdenum(VI) complexes with ONO–ONO-type hexadentate Schiff base ligands

The $^1$H NMR spectrum of the dinuclear *cis*-dioxomolybdenum(VI) complex containing the Schiff base ligand derived from 2,5-dihydroxyterephthalaldehyde and 2-amino-2-methyl-1,3-propanediol showed two sets of resonances. The ligand contains two prochiral carbon atoms, which become chiral (*R* and *S*) upon coordination. The combination of these two chiral centers generates three stereoisomers, *RR*, *SS*, and *RS* ( = *SR*), and the NMR characteristics were accounted for by these isomers.

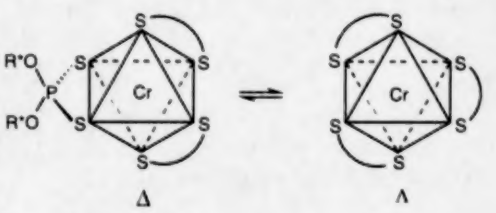



**Hiromi Ohta, Masakazu Kita, Hideaki Kanno, Masaaki Kojima**

*Inorg. Chim. Acta 311 (2000) 75*

Optically-active tris(*O*,*O*′-dialkyl dithiophosphato-*S*,*S*′)chromium(III) complexes. Isolation of diastereoisomers and isomerization reactions

Two optically-active *O*,*O*′-dialkyl dithiophosphate ligands, $(Bor)_2PS_2^-$ and $(Men)_2PS_2^-$, were prepared from $P_2S_5$ and the monoterpene alcohols, D-borneol and L-menthol. The diastereoisomers (Δ and Λ) of the chromium(III) complexes, $[Cr\{(Bor)_2PS_2\}_3]$ and $[Cr\{(Men)_2PS_2\}_3]$, were separated by fractional crystallization. The complexes were stereochemically nonrigid. Activation parameters for isomerization (epimerization), Δ → Λ and Λ → Δ were determined for both complexes, $[Cr\{(Bor)_2PS_2\}_3]$ and $[Cr\{(Men)_2PS_2\}_3]$. $[Cr\{(Men)_2PS_2\}_3]$ isomerizes much faster than $[Cr\{(Bor)_2PS_2\}_3]$.

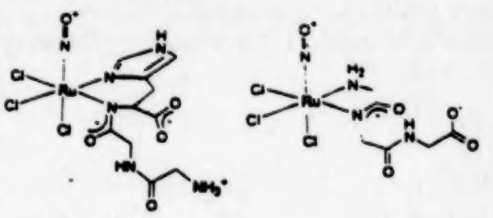



**Joseph M. Slocik, Rex E. Shepherd**

*Inorg. Chim. Acta 311 (2000) 80*

Coordination of $Ru(NO)Cl_3$ to the tripeptides gly–gly–gly and gly–gly–his: N-terminal amine–amide and C-terminal imidazole–amide functionalities in bidentate chelation

$[RuCl_3(NO)(H_2O)_2]$ reacts with triglycine (gly–gly–gly) to form complexes at pH ~ 8 predominantly coordinated through the N-terminal amino group and an adjacent, ionized amide donor that are cis to $NO^+$. The diglycylhistidine is coordinated via the imidazole (70%) with lesser amounts of a C-terminal imidazole–amide chelation (20%) and N-terminal amine–amide chelation (10%). The coordination chemistry is compared with that of $Pd^{II}$ and $Ni^{II}$ analogues.

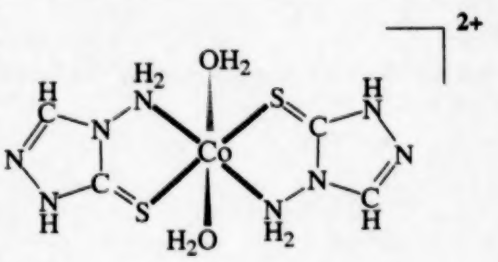


**Robert M. McCarrick, Martin J. Eltzroth, Philip J. Squattrito**

*Inorg. Chim. Acta 311 (2000) 95*

Coordination geometries of bis(4-amino-3-alkyl-1,2,4-triazole-5-thione) complexes of first-row transition metals: crystal structures of complexes with propyl and hydrogen in the 3-position. Relationship to the 3-methyl and 3-ethyl analogs

The chelating ligands 4-amino-3-propyl-1,2,4-triazole-5-thione (apt) and 4-amino-1,2,4-triazole-5-thione (aht) have been used to form a series of bis bidentate complexes with divalent Mn, Fe, Co, Ni, and Zn, extending the family of 4-amino-3-alkyl-1,2,4-triazole-5-thione complexes whose methyl and ethyl members have already been reported. All of the complexes contain two water molecules to complete the octahedral coordination sphere. Two geometries are observed, *cis* (point group $C_2$) and *trans* (point group $C_i$), based on the identity of the alkyl group, metal ion, and counter ion (either $NO_3^-$ or $ClO_4^-$).

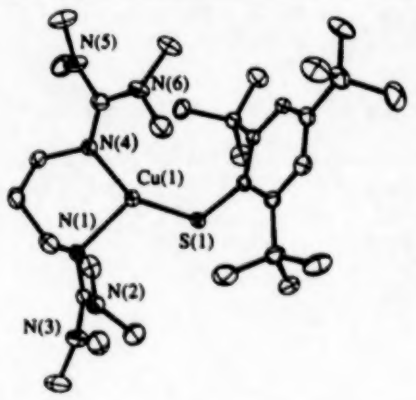



**Siegfried Pohl, Michael Harmjanz, Jörg Schneider, Wolfgang Saak, Gerald Henkel**

*Inorg. Chim. Acta 311 (2000) 106*

Syntheses and structures of transition metal thiolate complexes containing the new bis(tetramethylguanidine) ligand btmgp

The preparation and characterization of the first Cu(I)- and Fe(II)-thiolate guanidine complexes are described. The crystal structures of $[Cu(S\text{-}2,4,6\text{-}^tBu_3C_6H_2)(btmgp)]$ (**1**), $[Fe(S\text{-}2,4,6\text{-}^iPr_3C_6H_2)_2(btmgp)]$ (**2**) and $[Fe(SiMe_2(C_6H_4S)_2)(btmgp)]$ (**3**) [btmgp = 1,3-bis(*N*,*N*,*N*′,*N*′ - tetramethylguanidino) - propane] have been determined by X-ray diffraction. The X-ray structure analyses of **1**–**3** reveal trigonal planar (2N/1S) (**1**) and tetrahedral (2N/2S) (**2**, **3**) coordination environments around the metal centers.

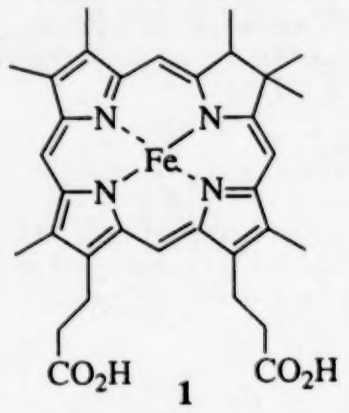


**Chariklia Sotiriou-Leventis, Chi K. Chang**

*Inorg. Chim. Acta 311 (2000) 113*

Kinetic study of CO and $O_2$ binding to horse heart myoglobin reconstituted with synthetic iron chlorin green hemes

Carbon monoxide- and oxygen-binding rates and affinities towards horse heart myoglobin reconstituted with synthetic iron chlorin (**1**) and iron oxo-chlorin green hemes were measured by flash photolysis and spectrophotometric titrations. In comparison with native myoglobin containing the red protoheme IX, these reconstituted green hemes exhibit faster association rates with both carbon monoxide and oxygen and lower affinities with oxygen.



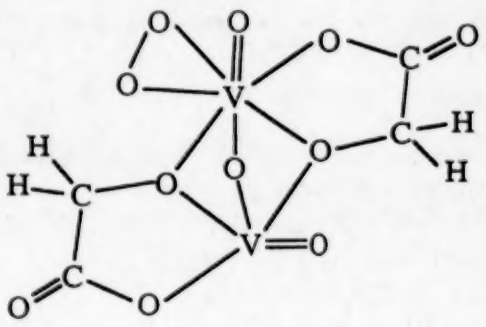
**1**

**Licínia L.G. Justino, M. Luísa Ramos, M. Madalena Caldeira, Victor M.S. Gil**

*Inorg. Chim. Acta 311 (2000) 119*

Peroxovanadium(V) complexes of glycolic acid as studied by NMR spectroscopy

NMR spectroscopy has been used to characterize the peroxovanadium(V) complexes of glycolic acid in aqueous solution. One 2:2:2 (metal:ligand:peroxo) complex, together with a 2:2:1 and a 1:1:1 species, are found in the pH range 1–7. The dinuclear and mononuclear complexes have, respectively, $V_2O_3^{4+}$ and $VO^{3+}$ metal centres.

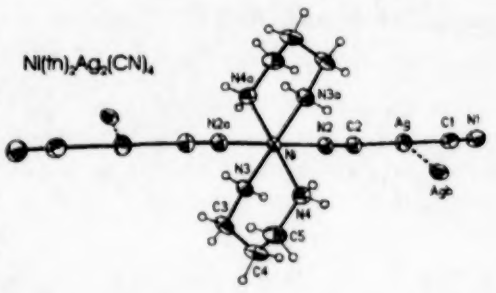



**J. Černák, K.A. Abboud, J. Chomič, M.W. Meisel, M. Orendáč, A. Orendáčová, A. Feher**

*Inorg. Chim. Acta 311 (2000) 126*

$Ni(tn)_2Ag_2(CN)_4$ and $Cu(tn)_2Ag_2(CN)_4$ (tn = 1,3-diaminopropane): preparation, crystal structure, magnetic and spectral properties

Two new compounds, $Ni(tn)_2Ag_2(CN)_4$ (tn = 1,3-diaminopropane) (NTAC) and $Cu(tn)_2Ag_2(CN)_4$ (CTAC), were prepared, and their structures were determined by single crystal X-ray diffraction. The paramagnetic central atoms are coordinated by two chelate bonded tn molecules and their coordination spheres are completed by two (Ni) and one (Cu) terminal diacyanoargentate anions, respectively. Short Ag···Ag contacts are present among anions. Susceptibility and magnetization studies revealed very weak exchange coupling in both compounds.



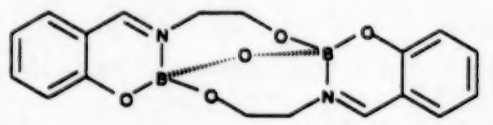

**Notes**

**Victor Barba, Gabriela Vargas, Elizabeth Gómez, Norberto Farfán**

*Inorg. Chim. Acta 311 (2000) 133*

A new oxo-bridged borate derived from dimeric boron complexes

The diborate compound, μ-oxo-$[B(SAE)]_2$ (**5**) was synthesized from dimeric boron derivatives obtained by reaction of the tridentate ligand ($H_2SAE$) with $B(NMe_2)_3$, $B(OH)_3$ and $C_6F_5B(OH)_2$. The structure of the oxo-bridged borate was established by crystallographic analysis and confirmed the existence of a B–O–B bridge.

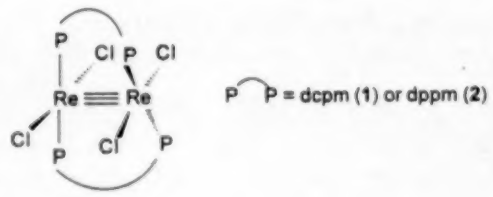



**Jitendra K. Bera, Phillip E. Fanwick, Richard A. Walton**

*Inorg. Chim. Acta 311 (2000) 138*

The structural characterization of $Re_2Cl_4(\mu\text{-dcpm})_2$ (dcpm = $Cy_2PCH_2PCy_2$) and a new crystallographic form of $Re_2Cl_4(\mu\text{-dppm})_2$ (dppm = $Ph_2PCH_2PPh_2$)

The reactions of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$ with $Cy_2PCH_2PCy_2$ (dcpm) and $Ph_2PCH_2PPh_2$ (dppm) in ethanol afford the complexes $Re_2Cl_4(\mu\text{-dcpm})_2$ (**1**) and $Re_2Cl_4(\mu\text{-dppm})_2$ (**2**). Both have been structurally characterized by X-ray crystallography, and this crystal form of **2** is different from that whose structure was reported previously.

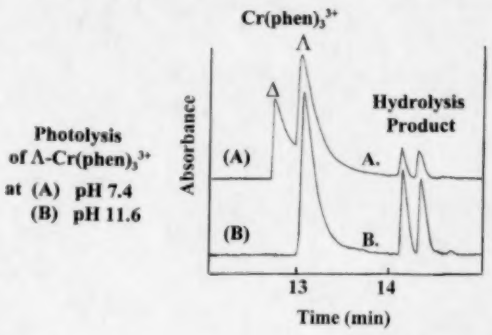


**Olga V. Mytykh, Susan E. Martin, John F. Wheeler, Noel A.P. Kane-Maguire**

*Inorg. Chim. Acta 311 (2000) 143*

Application of capillary electrophoresis to stereochemical conversions. A case study: the photoracemization/hydrolysis of $Cr(diimine)_3^{3+}$ species

Capillary electrophoresis studies on the photolysis of $\Lambda$-$Cr(bpy)_3^{3+}$ and $\Lambda$-$Cr(phen)_3^{3+}$ in acidic and basic solution support a mechanism where racemization and hydrolysis are competing processes involving a common intermediate.

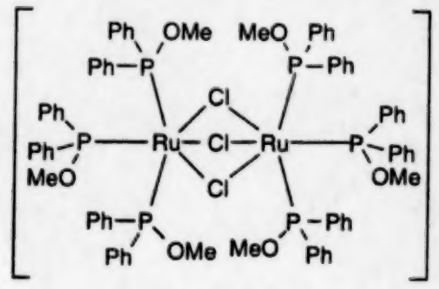



**Eric Dulière, Bernard Tinant, André Schanck, Michel Devillers, Jacqueline Marchand-Brynaert**

*Inorg. Chim. Acta 311 (2000) 147*

Synthesis, characterization, and catalytic behaviour of a dimeric ruthenium(II) methoxydiphenylphosphane complex

During the search for new ruthenium complexes to be used as alcohol oxidation catalysts, we synthesized dichlorotris(methoxydiphenylphosphane)ruthenium(II) which dimerizes. The structure of the dimer was established by NMR and X-ray diffraction analyses.

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